

ADHESION TENSION OF LIQUIDS AGAINST
STRONGLY HYDROPHILIC SOLIDS

A SERIES OF LIQUIDS AGAINST BARITE

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

BY

HARLEY YOUNG JENNINGS

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The object of the present investigation was to improve and simplify the pressure of displacement method for measuring adhesion tension (1, 3, 4, 6, 11, 12), to adapt it for use with softer and less rigid materials than had previously been employed, and to obtain additional adhesion tension data with hydrophilic solid systems. It had been found that maximum pressure values obtained with receding liquid columns were more reproducible and more readily obtained than those determined with advancing liquid columns (8, 9). Accordingly pressures were measured which were just sufficient to cause the liquid column in the compressed powder membrane to recede.

APPARATUS

Since it had been found that the original hydraulic press method of packing cells caused crushing or cleaving of solid materials such as barite, new methods of packing the compressed powder membrane were studied. A tamping method of packing was finally adopted. Reproducible results were obtained by tamping even when the tamping plunger was operated by hand. Identical volumes were obtained by tamping the powder wet or dry. Hand tamping had the disadvantage that the force of impact of the packing plunger could not be measured in definite units, hence one investigator had difficulty in reproducing the results of another. A mechanical tamping machine was constructed which could be regulated so as to give definite and reproducible degrees of packing.

The cell to be packed was placed on a base, mounted on a stiff coil spring, which vibrated with each impact of the plunger. A packing guide directed the packing plunger as it fell into the cell. The plunger was raised by a small chain which passed through a pulley mounted above the cell. The pulley was adjustable and its position determined the distance of fall of the plunger. A ratchet device attached to the chain released the packing plunger, which fell freely with each revolution of a hand-turned crank shaft. It was necessary to determine the weight of the packing plunger and the

distance of fall advisable for each solid. For the measurements with barite reported herein, a plunger weighing 360 g. was dropped 20 mm. fifty times with each added increment. About five 1-g. increments were used in the

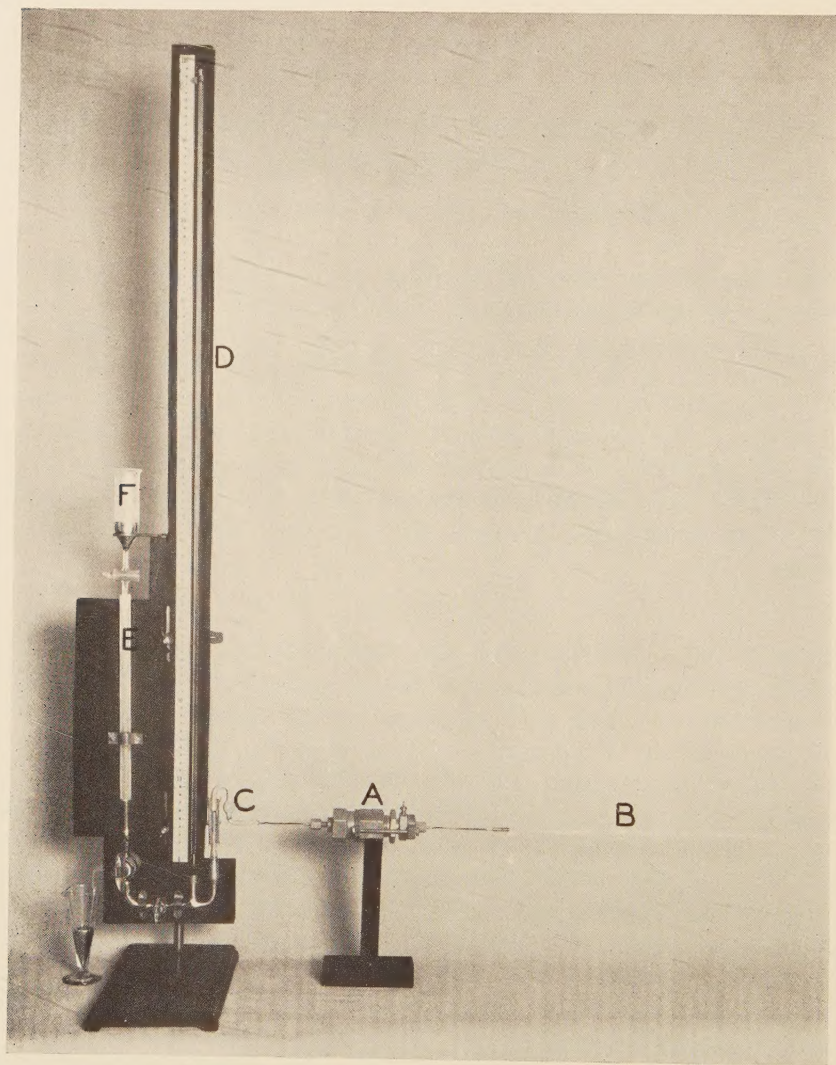


FIG. 1. CELL AND MANOMETER ASSEMBLY

A, displacement cell; B, indicator tube; C, bulb, intermediate section; D, manometer tube; E, auxiliary tube; F, mercury reservoir and drop control.

preparation of the membrane. A circular disc of linen cloth was placed in the cell before packing and a second disc was placed over the powder

during the tamping process and was left in place after the last tamping. The tamping method of packing eliminated almost entirely difficulties previously encountered which were traceable to improperly packed cells.

The displacement cell assembly used in this investigation is shown in figure 1. This apparatus is similar to that used by Bartell and Whitney (8). All measurements were made in a constant temperature thermostat held at $25^{\circ}\text{C.} \pm 0.1^{\circ}\text{C.}$

MATERIALS

The liquids used in this investigation were acetylene tetrabromide, benzene, carbon tetrachloride, heptane, butyl acetate and water. The liquids were all purified before use. In general, the purification was not rigorous, but was sufficient to give a reasonably pure product. The surface and interfacial tension values were determined for all the liquids.

The solid used was mineral barite, which contained less than one per cent of silicious material. The barite was heated in an electric oven for two hours at 400°C. and then ground in a ball mill. It was then washed with acetone (the very fine material was removed by decantation), dried for three hours at 110°C. , and finally sifted through a series of screens to give definite particle size, 200 to 300 mesh.

METHOD OF MEASUREMENT

The graded powder was packed dry into the cell by tamping. The cell plunger was put in place and securely fastened. The liquid to be used was then drawn into the cell by suction until the powder was completely wetted, and the liquid column was caused to extend from the cell into the capillary indicator tube. For the pressure of displacement measurement of liquid-air systems the pressure was slowly built up by very fine drops of mercury which were caused to fall into the auxiliary arm E of the manometer D (see figure 1). As soon as the movement of liquid outward in the indicator tube was definite and constant, the auxiliary arm of the manometer was closed, leaving the manometer directly connected to the cell. The pressure in the manometer now continued to decrease as the liquid-air interface continued to move outward. Finally movement of the liquid column ceased and the pressure remained constant. This pressure was readily reproducible and was taken to represent the equilibrium pressure. The most consistent results were obtained when the interface was caused to come to rest near the middle of the membrane.

Measurements with liquid-liquid systems were carried out in a similar manner. The membrane was first wetted with the displacing liquid (for hydrophilic solids, water). In this case the indicator tube, B, was left full of liquid. The second liquid (organic liquid) was put into the glass bulb, C, which formed the intermediate section between the cell and manometer.

It was necessary to eliminate air completely from the liquid-liquid interface. This was accomplished by making a connection to the end of the indicator tube and applying enough pressure to cause the liquid in the cell to move through the small metal tube leading to the intermediate section. This section containing the organic liquid was tilted so as to bring the two liquids together and the interface, now free from air, was forced back into

TABLE 1
Adhesion tension measurements with barite
Air-organic liquid-barite
 $r = 1.43 \times 10^{-3}$ cm.

LIQUID	P	$\cos \Theta_{12}$	Θ_{12}	S_2	A_{12}
	<i>grams per cm².</i>				
Acetylene tetrabromide.....	57.7	0.822	34°	49.07	40.5
α -bromonaphthalene.....	56.9	0.909	25°	44.00	39.9

P = Displacement pressure.

Θ_{12} = Contact angle solid-organic liquid-air.

Θ_{23} = Contact angle solid-organic liquid-water.

S_2 = Surface tension organic liquid.

S_{23} = Interfacial tension organic liquid against water.

A_{12} = Adhesion tension organic liquid against solid.

A_{13} = Adhesion tension water against solid.

TABLE 2
*Adhesion tension measurements with barite**
Water-organic liquid-barite

LIQUID	P	$\cos \Theta_{23}$	Θ_{23}	S_{23}	A_{12}	A_{13}
	<i>grams per cm².</i>					
Acetylene tetrabromide.....	50.7	0.928	22°	38.32		76.1
α -Bromonaphthalene.....	52.3	0.883	27°	41.57		76.6
Benzene.....	45.7	0.935	21°	34.31	44.3	
Heptane.....	61.8	0.877	28°	49.40	33.1	
Butyl acetate.....	16.8	0.896	26°	13.17	64.6	

* See footnote to table 1.

the membrane. Final connections to the manometer were made by means of ground glass joints and the procedure from this point was exactly the same as described for liquid-air systems.

DISCUSSION OF RESULTS

A summary of the adhesion tension values obtained for the different liquids against barite is given in tables 1 and 2. Each of the values is

the average of several separate determinations. The equations used and methods of calculating results have been presented in previous articles from this laboratory. The three liquids, benzene, carbon tetrachloride, and water were used to determine the pore radius (r). The radii as determined with these liquids showed excellent agreement. The adhesion tension values obtained for the series of liquids against barite were of the same order of magnitude as those which had been obtained for these liquids against silica (8) and against aluminum oxide (7). Table 3 gives the adhesion tension values obtained with five different liquids against these three different solids. In checking the data obtained in two hundred thirty-three different measurements made with these three different solids by the receding contact angle method, it was found that the largest average deviation in any one system was less than 1.5 per cent.

TABLE 3
Comparison of adhesion tension values for hydrophilic solids

SOLIDS	α - BROMO- NAPH- THALENE	ACETY- LENE TETRA- BROMIDE	BENZENE	BUTYL ACETATE	WATER
Barite.....	39.9	40.5	44.3	64.6	76.4
Aluminum oxide (7).....	40.1	43.0	45.0	64.5	76.7
Silica (8).....	39.6	42.8	44.1	64.5	76.7
Silica (2) (Single capillary method)....	41.1	43.3	45.4	66.6	75.9
Calcium fluoride (1).....	43.0	—	50.1	65.2	76.5

The fact that these hydrophilic solids tend toward similar adhesion tension values indicates that they possess free surface energy values of the same order of magnitude.¹ It has been noted also that these solids exhibit similar behavior in settling experiments. With a series of liquids the degree of packing of the powders of these different solids on settling is always in the same order and usually of the same magnitude. It would be unreasonable to assume that all the solids per se possess the same free surface energy values. It would be more reasonable to assume that their surfaces when exposed to atmospheric conditions become altered. Probably water vapor

¹ Bartell and Osterhof (5) have pointed out that the adhesion tension values which they obtained for different liquids against Tripoli, based on a water-Tripoli value of 81.5 dynes, are about 6 dynes higher than the values obtained with the same liquids against other silicas by other investigators (2, 8). Their value of 81.5 dynes was established with the use of only one contact angle liquid, α -bromonaphthalene. We are inclined to believe that this one measurement is in error, inasmuch as the values they obtained with other liquids (assuming the reference value above mentioned to be in error) are similar to those obtained by other investigators. If it be true that this value is in error, it follows that the adhesion tension values of all the hydrophilic solids measured thus far give values of approximately the same magnitude.

is adsorbed. We are led to agree with other investigators (10, 13, 15, 16) that a primary water film is tenaciously adsorbed on the surface of hydrophilic solids and that the water molecules are definitely oriented.

Although considerable care has been exercised in all the displacement pressure researches in this laboratory to produce a reasonably clean surface on the solids used, it is doubtful if the procedure followed has prevented the formation of a water film (which may or may not be complete, i.e., it may be polymolecular or even monomolecular in thickness) on the capillary surfaces of the powdered membrane at some time before the final measurement was made. With the barite and aluminum oxide investigations conditions were certainly favorable for the formation of a complete water film, for the equilibrium pressure measurements were made by forcing the organic liquid into membranes which were already wetted by water. Under these conditions, however, it could be shown experimentally that this film was such that it possessed properties different from those of a liquid in mass. For example, when the organic liquid was forced into the water-wet barite membrane rapidly by building up an opposing pressure considerably above the equilibrium pressure and then the system allowed to come to an apparent equilibrium, in a short time a pressure was obtained which was the same as the pressure value demanded by a zero interfacial angle, that is a value of $A_{13} - A_{12}$ equal to the interfacial tension value of the organic liquid-water system was obtained. This indicated the presence of a complete water film, having the properties of a plane surface of water. In other words, this procedure gave a method, as had been previously pointed out (8), for measuring interfacial tension of organic liquid against water in water-wet capillaries. On the other hand, if the opposing pressure was built up slowly so that the organic liquid displaced the water slowly and the equilibrium pressure was only slightly exceeded, then a stable equilibrium condition was finally reached at a pressure lower than that demanded by the interfacial tension value. This indicated that a finite contact angle had formed and indicated further that no complete water film was present which possessed the property of a plane surface of water. The values given in tables 1 and 2 were obtained by the latter method.

It has previously been shown (2, 8) that the same values for adhesion tension of a given organic liquid against a solid are obtained by measurement of the solid-organic liquid-air contact angle as are obtained by measurement of the solid-organic liquid-water contact angle. The question may be raised as to the reliability of the adhesion tension data obtained with the pressure of displacement method, particularly with solids whose surfaces are not distinctly free from water films. Will data obtained enable one to detect differences in surface conditions of a strongly hydrophilic solid? The answer is that the data obtained are indicative of the nature of the surfaces as they actually exist, and that such data do enable one to predict the behavior to be expected with solids possessing such surfaces.

SUMMARY

A modification of the original pressure of displacement method for determining adhesion tension, termed a receding contact angle method, is described in some detail. This method is far more rapid, is easier to operate, and can be used with less danger of experimental error than the original method. An improved method is described for the preparation of membranes from finely divided powders. This method involves packing of powder by tamping. A tamping apparatus is described which gives a uniformly packed powder. The adhesion tension value of each of a series of liquids against barite is given. Comparison of the adhesion tension values of each of a series of liquids against each of several different hydrophilic solids shows that corresponding values are of very nearly the same magnitude. From this fact the conclusion is drawn that the surfaces of strongly hydrophilic solids are covered with an adsorbed film of water which gives to these solid surfaces such properties that their measured free surface energy values are of the same order of magnitude.

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